

Synthesis and Characterization of Segmented Polyurethanes Containing Polyhedral Oligomeric Silsesquioxanes (POSS) Nanostructured Molecules

B. Fu, W. Zhang, B. Hsiao, M. Rafailovich, J. Sokolov, (SUNY, Stony Brook), J. Johansson, B. Sauer, (DuPont de Nemours and Co), S. Phillips, and R. Balnski (Air Force Research Lab)

Abstract No: Fu9006

Beamline(s): **X3A2**

Introduction: the properties of polyurethane are primarily related to the formation of microphase separation from the thermodynamic incompatibility (immiscibility) of solid-like hard segments and rubbery soft segments. The hard segments usually involve the interchain interactions by means of van der Waals forces and hydrogen bonding, which determine the macroscopic properties. In this study, we have investigated a polyurethane system with the hard segments being molecularly modified by nanostructured molecules – polyhedral oligomeric silsesquioxanes (POSS). The POSS molecule contains a polyhedral silicon-oxygen nanostructured skeleton with intermittent siloxane chains (general formula $(\text{SiO}_{3/2})_n$) and having one corner attached to a functional organic group R. Different POSS molecules have been successfully incorporated into many kinds of polymers such as styryls, acrylics, liquid crystalline polyesters, siloxanes, and polyamides⁴⁻⁷. Previous studies showed that the resultant polymers are hybrid organic-inorganic nanostructured composites exhibited improved properties in T_g , oxygen permeability, flammability retardation and mechanical strength.

Methods and Materials: In this study, a series of polyurethane with inorganic POSS molecules incorporated into the hard segments was synthesized and characterized by means of differential scanning calorimetry (DSC), tensile mechanical tests, simultaneous wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) techniques. Samples molecular weights were determined by gel permeation chromatography (GPC).

Results: Microphase separation between the hard and soft segment domains was observed in all the samples by SAXS. The increase of POSS concentration was found to weaken the microphase separation between the domains and increase the T_g of soft segments. The WAXD results showed that when the POSS concentration became larger than 10 wt%, the 101 diffraction peak from the POSS crystals could be observed, which suggested the formation of POSS nanocrystals in the hard domain. The tensile property tests showed that polyurethanes containing the nanostructured POSS molecules had higher modulus but lower maximum elongation ratios.

Conclusions: A series of polyurethanes containing different composition of POSS molecules was synthesized and investigated by means of GPC, DSC, tensile mechanical tests and simultaneously WAXD and SAXS techniques. The DSC scans showed an increase of T_g in the soft segment with the increase of POSS concentration. This suggests that the POSS inclusion causes an increase in the miscibility between the soft and hard segments leading to the formation of a segment polymer with lesser microphase separation, which was further supported by SAXS. The WAXD profiles showed that when the POSS content was high enough (10wt%), POSS molecules could form nanocrystals in the polymer matrix, exhibiting a crystal reflection peak at 11.3 Å in d-spacing. The tensile property tests showed that polyurethanes containing POSS molecules generally have higher modulus but lower maximum elongation ratios, which can be attributed to the attachment of rigid POSS molecules at the molecular level and the improved miscibility between the hard and soft segments.

Acknowledgments: We would like to acknowledge the financial support of this work by a Young Faculty Grant from DuPont and in part by NSF-MRSEC (DMR9632525) and by the Air Force Research Lab. We thank Dr. Zhigang Wang and Dr. Shaofeng Ran for their helpful assistance in this study.